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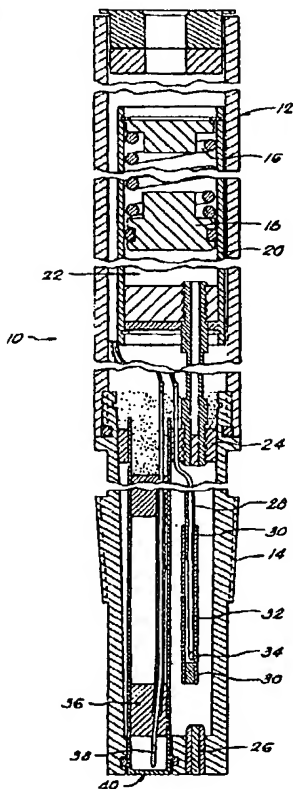
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- (71) Applicant (for all designated States except US): **THE FOXBORO COMPANY** [US/US]; 33 Commerical Street, Foxboro, MA 02035 (US).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **FLETCHER, Kenneth, S.** [US/US]; 101 Roger Street, Hartford, CT 06106 (US). **SKINNER, David, N.** [US/US]; 18 Riverside Avenue, Milton, MA 02189 (US). **CANDELA, Ellen** [US/US]; 116 Pleasant Street, Cohasset, MA 02025 (US). **BOWER, Michael, M.** [US/US]; 4 Lake Shore Drive, Wareham, MA 02571 (US).
- (74) Agents: **LIEPMANN, W., Hugo et al.**; Patent Group, Foley, Hoag & Eliot LLP, One Post Office Square, Boston, MA 02109-2170 (US).
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(54) Title: **SENSOR FOR ELECTROCHEMICAL MEASUREMENT**

(57) Abstract: The invention provides a sensor with a reference electrode and a flowing electrolyte which is particularly useful for measuring the ion concentration of a process solution. The invention includes a sensor having a pressurized reservoir which provides flow of an electrolyte, a non-metallic solution ground and a resistance temperature device bonded to a non-metallic solution ground. The invention provides sensors with greater accuracy and stability by minimizing or eliminating ingress of contaminants from a process solution through the external junction of the sensor.



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INTERNATIONAL SEARCH REPORT

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A		2,3,5-8, 10-36, 38-48, 52-72
X	US 3 445 368 A (DETEMPLE MANFRED) 20 May 1969 (1969-05-20) the whole document	1,4,9, 37,49-51
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Savage, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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(71) Applicant
Corning Glass Works,
Corning,
New York 14831,
United States of America

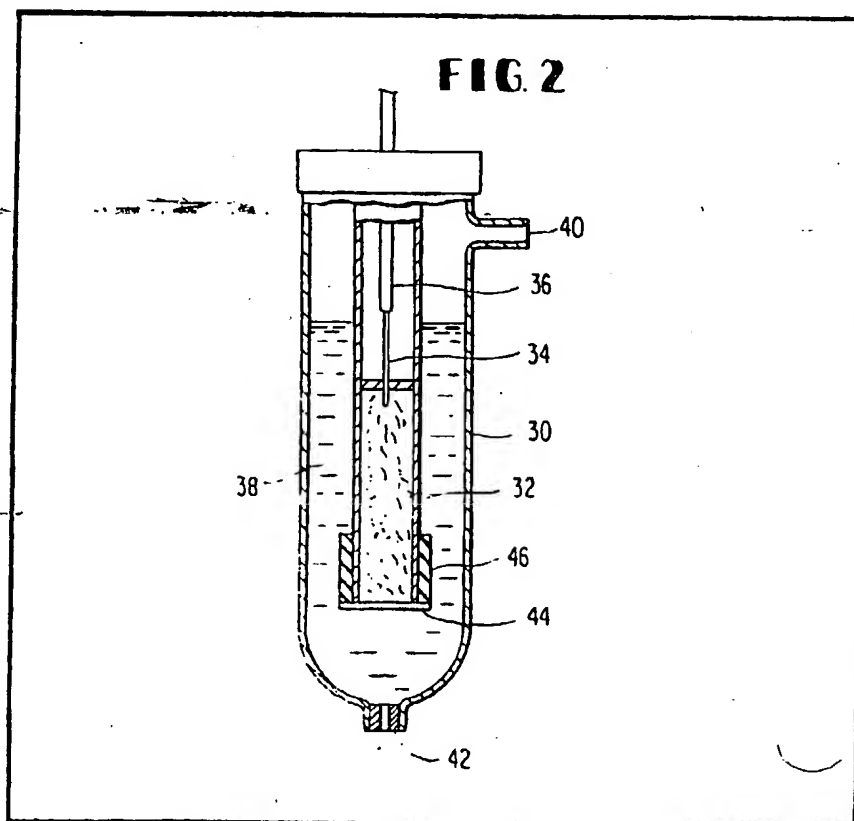
(72) Inventor
Donald Peter Brezinski

(74) Agents
Elkington & Fife,
High Holborn House,
52/54, High Holborn,
London,
WC1V 6SH

(54) Reference Electrode with
Internal Ion-selective Barrier

(67) A reference electrode having a double junction configuration comprises, a first housing containing an electrochemical half-cell (32) being electrically connectable by means of a wire (34) and insulated conductor (36) to an external measuring means and consisting essentially of a half-cell electrode and a half-cell electrolyte, a second housing containing a junction

electrolyte (38), an ion selective barrier (44) which allows desired ion migration to maintain an ionic electrical pathway between said half-cell electrolyte and said junction electrolyte and which substantially prevents undesired ion migration, thereby substantially preventing contamination of said junction electrolyte with undesired ions; and a reference junction (42) allowing ionic conduction between said junction electrolyte and an external sample to be measured.



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FIG. 1

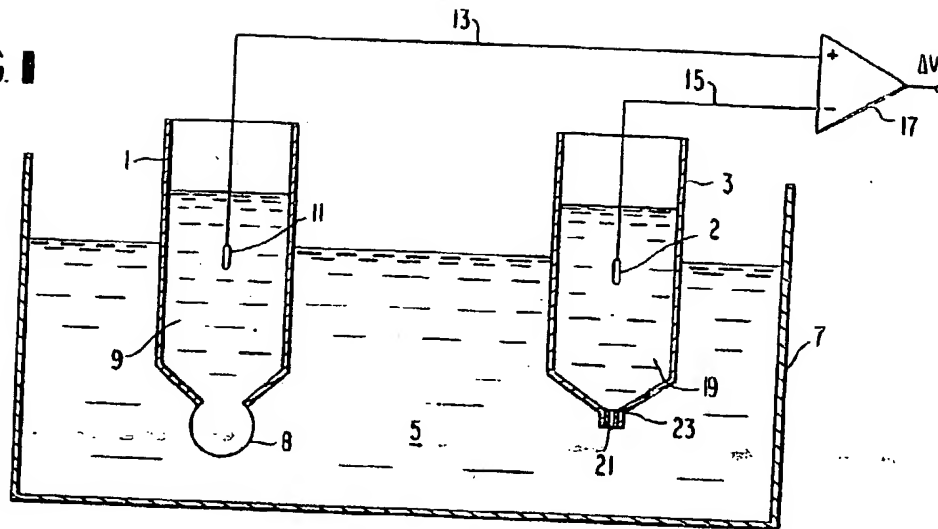


FIG. 2

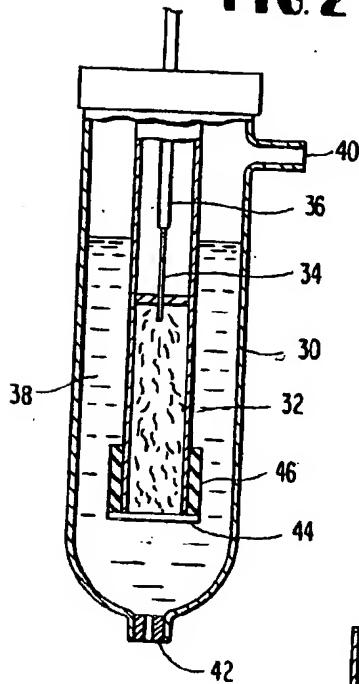


FIG. 3

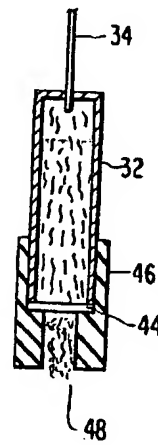


FIG. 4

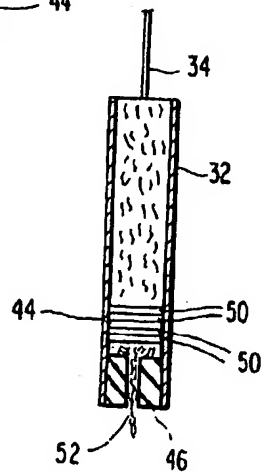
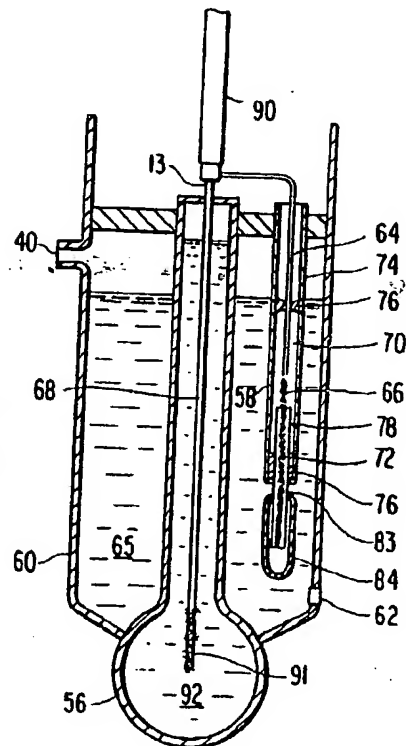


FIG. 5



SPECIFICATION

Reference Electrode with Internal Ion-Selective Barrier

5 The present invention is concerned with reference electrodes, and the reference electrode portion of combination electrodes, which are employed to provide the stable reference potentials required by a variety of electroanalytical techniques, such as ion-selective coulometry, polarography, and the like. More particularly, the present invention is concerned with what commonly are referred to in the art as double junction reference electrodes.

10 A reference electrode most frequently is used in conjunction with an ion-selective electrode, either separately or in combination, to measure the activity (which is a function of concentration) of a given ion in a sample solution. Consequently, the discussion which follows primarily relates to such use. It is to be understood, however, that such discussion is not intended to in any way limit the spirit or scope of the present invention.

15 The two electrodes, i.e. the reference electrode and the ion-selective electrode, both of which are immersed in the sample solution, typically are connected to a means for measuring the potential difference between the electrodes, e.g. an electrometer. The reference electrode provides a constant electromotive force or potential against which the potential of the ion-selective electrode is compared. The latter potential consists of a constant component from the electrochemical half-cell of the ion-selective electrode and a variable component which is the potential across the sensing membrane and which is dependent upon the activity (concentration) of the ion being measured. The variable component, then, is readily correlated with ion activity (concentration) by known means. To give accurate results, the potential of the reference electrode should not change with the composition of the sample.

20 The reference electrode is designed to be minimally sensitive to changes in the external, sample ionic environment. It consists of at least three components; (1) a half-cell electrode (typically a silver-silver chloride mixture), (2), a half-cell electrolyte (typically 4M potassium chloride solution saturated with silver ions), and (3) a reference junction. The half-cell electrode and half-cell electrolyte constitute an electrochemical half-cell having a known, stable, constant electrical potential. Direct physical, and therefore electrical, contact between the half-cell electrolyte and the sample solution is established through the reference junction which usually consists of a porous ceramic plug, metal or asbestos fibre bundle, sintered plastic, or like means of achieving a fluid mechanical leak.

25 As used herein, the term "half-cell electrode" means the solid-phase, electron-conducting contact with the half-cell electrolyte, at which contact the half-cell oxidation-reduction reaction occurs which establishes the stable potential

65 between the half-cell electrolyte and the contact.

A major disadvantage of conventional reference electrodes of the above-described type is that the same electrolyte is used to accomplish two unrelated tasks; (1) setting the potential of the electrochemical half-cell, and (2) establishing contact with the sample solution via the reference junction. Half-cell ions, such as Ag^+ in an Ag/AgCl electrode, Hg^+ in a calomel electrode, and Tl^+ in a thallium amalgam electrode, are also present at the reference junction where they may contaminate the measured solution and, in certain circumstances, precipitate, clogging the junction.

70 For example, one of the major deficiencies of Ag/AgCl electrodes is the tendency of AgCl or other silver salts to precipitate within the junction, clogging it and interfering with free diffusion between the measured solution and internal electrolyte. Manifestations of a clogged reference junction include slow response, stirring-dependent potentials, and erroneous potentials at equilibrium.

75 Clogging increases response time by stopping the outward flow of junction electrolyte. In the absence of outward flow, the measured solution diffuses deep into the reference junction and temporarily serves as the junction electrolyte when the next solution is measured. The result may be a large diffusion potential which persists until the old sample is cleared from the junction by diffusion. With adequate outward flow, response time is minimized since the measured solution cannot penetrate deep into the junction and is flushed rapidly away during the next measurement.

80 Clogging by AgCl or other heavy metal salts may also cause non ideal response in low ionic strength samples. This results in static error (due to the shift in potential upon entering the charged junction), stirring effects (due to shifts in static error with local changes in electrolyte concentration at the junction surface) and flow-dependent potentials (due to streaming potentials generated within the junction).

85 The tendency of the Ag/AgCl electrode to clog is particularly unfortunate, since it otherwise is an excellent electrode that offers high stability, ease of manufacture, low toxicity and extended temperature range.

90 AgCl tends to precipitate in the junction because AgCl is much more soluble in the usual 4M KCl internal electrolyte than in the solutions in which the electrode is usually immersed. While the solubility of AgCl in pure water is very low, about $1.3 \times 10^{-5} \text{M}$, the solubility of AgCl in 4M KCl is about 500-fold higher, around $7 \times 10^{-3} \text{M}$. This high solubility is attributable to the formation of negatively charged ionic complexes between Ag^+ and Cl^- having the general form $\text{Ag}_n\text{Cl}_{n+1}^-$. When AgCl -saturated 4M KCl flows or diffuses into a more dilute solution, the Cl^- concentration is reduced and the excess silver chloride is precipitated. Precipitation of silver salt is often evident as a darkening of the external surface of

the reference junction element and is particularly noticeable on older ceramic junctions.

Our experiments indicate that junctions of conventional Ag/AgCl electrodes clog very rapidly. Even a new electrode can lose most of its flow capability after less than 24 hours in solution.

Contamination of the measured solution by heavy metal ions in the junction electrolyte is another problem associated with conventional reference electrodes. While silver is not particularly poisonous, its presence could be a problem in certain applications, e.g. photographic and forensic chemistry. Tl^+ and Hg^+ ions are very poisonous, and Hg^+ has been observed to inhibit a variety of enzymatic reactions.

Metal salts cannot simply be omitted from the electrolyte of conventional reference electrodes since they are required to establish a stable electrode potential. Even if the metal salt is initially located only at the half-cell electrode or contact, as in an AgCl-dipped silver wire, the salt will dissolve and quickly spread by diffusion and convection until the electrolyte is saturated.

Deliberate confinement is required.

One approach to eliminating undesired ions in the junction electrolyte is to use a so-called "double junction electrode" in which separate compartments containing the reference-junction and half-cell electrolytes are connected by an internal liquid junction provided by, for example, a porous ceramic plug. Double junction electrodes are widely used in ion-selective electrode measurements where it is desirable to use a salt other than KCl as the junction electrolyte, but have not been generally used for the specific purpose of excluding heavy metal ions from the junction electrolyte. Nevertheless, they could be used for the latter purpose. However, there are problems with conventional double junction electrodes. In most double junction electrodes, the inner junction is fairly permeable to flow under pressure. By design, the inner half-cell compartment is refillable and the half-cell electrolyte flows under gravity through the inner junction into the junction electrolyte. This requires periodic refilling of the inner half-cell electrolyte and causes contamination of the external junction electrolyte. Even if the inner compartment is sealed, mixing between inner and outer electrolytes can occur as a consequence of diffusional interchange or bulk flow through the inner junction due to pressure gradients brought about by thermal expansion or changes in ambient pressure.

Additionally, the conventional double junction electrode configuration necessitates a compromise between the electrode's diffusional-exchange and electrical-noise characteristics. As we have discussed in co-pending application Serial No.

of even date and entitled "Reference Electrode with Internal Diffusion Barrier", we have found that the rate of diffusional exchange of an electrolyte through a porous barrier is inversely proportional to the electrical resistance of the

barrier, but is independent of the barrier's size, shape or structural detail. (The resistance of the barrier can be measured by saturating it with the electrolyte under consideration, applying a voltage, and determining the ratio of applied voltage to the resulting ionic current). Thus, the effectiveness of a diffusion barrier is completely characterized by its electrical resistance, which usually must be appreciable to adequately retard diffusional mixing of electrolytes. But the high resistance required of an effective diffusion barrier contributes to the electrical noise susceptibility of the reference electrode. Thus, we have found that for conventional double junction electrodes, there is necessarily a reciprocal relationship between noise-causing barrier resistance and diffusional transport across the barrier.

It is an object of this invention to provide an improved reference electrode.

A more specific object of this invention is to prevent heavy metal ions of an electrochemical half-cell in a reference electrode from clogging the reference junction or contaminating the measured solution.

A yet more specific object of this invention is to provide an improved reference electrode which includes separate half-cell and junction electrolytes and a means to selectively prevent ionic contamination of junction electrolyte by ions migrating from the half-cell electrolyte.

A further object of this invention is to substantially prevent undesired migration of ions between the half-cell and junction electrolytes of a reference electrode without substantially increasing the electrical resistance thereof.

Still another object of this invention is to provide an improved reference electrode characterized by improved potential stability, reproducibility, quick response, less drift, and reduced thermal hysteresis.

These and other objects will be readily apparent to those skilled in the art from a consideration of the specification and claims which follow:

Accordingly, the present invention provides a reference electrode having a double junction configuration and comprising a first housing containing an electrochemical half-cell being electrically connectable to an external measuring means and consisting essentially of a half-cell electrode and a half-cell electrolyte, a second housing containing a junction electrolyte, an ion selective barrier which allows desired ion migration to maintain an ionic electrical pathway between said half-cell electrolyte and said junction electrolyte and which substantially prevents undesired ion migration, thereby substantially preventing contamination of said junction electrolyte with undesired ions; and a reference junction allowing ionic conduction between said junction electrolyte and an external sample to be measured.

In preferred embodiments of the present invention, the ion-selective barrier can be an ion

exchange membrane which is cationic, anionic or specific ion selective.

In preferred embodiments of the present invention, the ion-selective barrier comprises a

5 chemically inert backbone polymer having dangling acid groups, particularly sulfonic acid groups, to significantly reduce negative ion migration through the barrier.

In a very preferred embodiment of the

10 invention, the barrier is not only an ion-exchange membrane, but is also of a sufficiently small pore size to physically reduce undesired ion migration and liquid flow therethrough.

The use of an ion-exchange membrane as a salt bridge is cited in the prior art, see, e.g. W. M. Carson et al, Anal. Chem, 27, 472 (1955). However, such prior use differs from the present invention in several significant aspects, as

15 discussed below.

In the above reference, the ion-exchange membrane was used as the reference junction of a single-junction reference electrode to provide a salt bridge between the external solution to be measured and the half-cell electrolyte. In the

20 present invention, the ion-exchange material is used as the inner junction of a reference electrode having a double junction configuration; consequently, such junction does not come into direct contact with the sample solution. This

25 difference in configuration allows much improved electrode performance, since the performance requirements of the inner junction and outer junction are quite dissimilar and therefore benefit from separate optimization.

In actual practice, ion-exchange membranes are quite unsuitable for use as general purpose reference junctions as disclosed in Carson et al., supra, since the potential across such a

30 membrane depends markedly on the generally unknown ionic composition of the sample solution. This defeats the purpose of the reference electrode, except in specialized applications where the general ionic background is held constant. Also, the potentials across general

35 cation- or anion-exchange membranes tend to drift after large changes in ionic environment due to non-uniform specificity among different ions of like charge, so such junctions often would fail to even provide a steady, if unknown, potential.

These disadvantages are overcome in the present invention by exposing the ion-selective barrier to an intermediary junction electrolyte of fixed

40 composition rather than directly to the sample solution. The reference junction itself then can be designed for optimal response characteristics.

45

Other particularly novel aspects of the present invention include the following. Since the deleterious effects of AgCl clogging of the reference junction have not been adequately

50 appreciated, the advantages of an Ag/AgCl reference electrode with a silver-free junction electrolyte was not previously apparent. The use of a cation-exchange barrier in blocking soluble silver is a novel approach which depends on the

55 atypical negative charge of the soluble silver

complex. The high barrier efficiency of a perfluorosulfonic acid membrane to soluble silver is surprising in view of the membrane's limited permselectivity at high KCl concentrations.

In the accompanying drawings:

Figure 1 is a schematic of a typical pH measurement system, illustrating the essential components thereof,

Figure 2 depicts in cross section one embodiment of the reference electrode of the present invention,

Figure 3 depicts in cross section a second embodiment of the reference electrode of the present invention,

Figure 4 depicts in cross section a third embodiment of the reference electrode of the present invention, and

Figure 5 depicts in cross section a combination electrode of the present invention including a preferred embodiment for the reference electrode portion thereof.

Figure 1 illustrates the essential elements of a typical pH measurement system. pH electrode 1 and reference electrode 3 are partially immersed

60 in sample solution 5 in container 7 and both electrodes are electrically connected to electrometer 17 by conductors 13 and 15. The potential across the glass sensing-membrane 8 of the pH electrode changes in proportion to the difference in pH between external sample solution 5 and a pH buffer solution 9 contained within the sensor membrane. An electrochemical half-cell 11 is used to establish a stable electrical connection between the inner buffer solution 9 and the wire conductor 13 leading to the

65 electrometer. This half-cell has a fixed potential determined by the anion concentration of the buffer solution. The difference in potential between the external solution 5 and the positive electrometer terminal changes with pH, and it is this change in potential that is to be monitored. The role of the reference electrode is to establish a fixed half-cell potential between the external measured solution and the negative electrometer terminal. In measurements of unknown solutions, the half-cell cannot be directly immersed in the sample, since its potential will vary with the unknown anionic activity of the solution. Therefore, an indirect reference connection is made by immersing the reference half-cell 2 into a known electrolyte 19 and then establishing physical and electrical contact between this electrolyte and the measured solution through a reference junction 21 positioned in outlet 23 of the electrode envelope. The reference junction usually consists of a porous ceramic plug, asbestos fibre, or other means of achieving a fluid mechanical leak. The reference junction functions primarily as a flow restrictor and filtration member, and also serves to define the shape of the interface between the solutions. Ideally, the junction is sufficiently porous to allow a low resistance contact between the external and internal solutions, preferably well below 10K ohm, but is not so porous that the solutions

become mutually contaminated. As already indicated and by way of illustration only, the half-cell electrode and half-cell electrolyte of the reference electrode typically are silver-silver chloride and AgCl-saturated 4M KCl, respectively. Similarly, the half-cell electrode and half-cell electrolyte of a typical pH electrode are silver-silver chloride and a buffer solution containing 0.1M chloride, respectively.

In each of Figures 2, 3 and 4, reference electrode 30 includes an electrochemical half-cell 32 consisting of a porous mixture of Ag and AgCl granules wetted with AgCl-saturated 4M KCl, which is connected by means of a wire 34 to an insulated conductor 36 which is connected to an electrometer, not shown. Junction electrolyte 38 can be added to the electrode through inlet 40 and can communicate with an external sample, not shown, through reference junction 42. In Figures 3 and 4, only the electrochemical half-cell 32 and wire 34, along with the improvement details of the present invention, are illustrated.

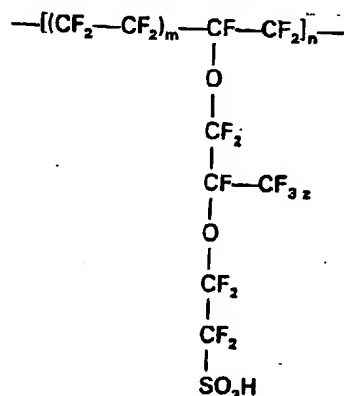
In Figures 2, 3 and 4, 44 is the ion-selective barrier used in this invention, while 46 is silicone rubber tubing. In the Figure 3 embodiment, the ion-selective barrier is positioned above cotton plug 48, while in Figure 4, two layers of filter paper (Whatman #1) 50 are on each side of the ion-selective barrier, with cotton plug 52 positioned below and against the ion-selective barrier-filter paper layers and extending through silicone tube 46.

In Figure 5, both the pH electrode and the reference electrode elements are incorporated into the same housing, thereby constituting a combination electrode configuration. The pH sensing portion of the electrode comprises the following: the inner conductor 13 of coaxial cable 90 is connected via silver wire to a half-cell consisting of a porous Ag/AgCl contact mass 91 immersed in a chloride-containing, pH buffered solution 92 within the pH sensor bulb 56. The reference electrode portion, which illustrates the most preferred configuration of the present invention, comprises the following elements: porous reference junction 62 allows ionic conduction between junction electrolyte 65 (pure 4M KCl in the preferred embodiment) and a sample solution, not shown. Silver wire 64 runs from the outer (braided shield) conductor 68 of the coaxial cable 90 to an electrochemical half-cell comprised in a preferred embodiment of a porous Ag/AgCl contact mass 66 immersed in half-cell solution 70 (AgCl-saturated 4M KCl in the preferred embodiment). The upper portion 72 of the electrochemical half-cell mass is positioned within glass capillary tube 74, sealed at the top and bottom by sealant 76. Ion-selective membrane 78 surrounds the contact mass 66 except for the uppermost portion thereof. The ion-selective membrane with included contact mass extends through sealant 76 at the bottom of the capillary tube down into the junction electrolyte 65. However, nearly all of the portion of membrane 78 extending beyond the capillary

tube is sealed by a water-resistant material 84, such as a water resistant epoxy, so that ionic conduction between the half-cell electrolyte 70 and junction electrolyte 65 occurs only through the membrane 78 at window 83.

The construction of reference electrode 58 will now be described in detail.

Wet-surface patching epoxy (Epoweld 3673) was obtained in Double/Bubble packets from Hardman, Inc. Belleville, NJ. Dow Corning 734 RTV adhesive/sealant (self-leveling one part silicone rubber, clear) was obtained from Summit Distributors, Buffalo, NY. NAFION 815 tubing (1.0 mm I.D. x 1.25 mm O.D.) was obtained from E.I. duPont de Nemours Co., Polymer Products Department, Wilmington, DE. Silver wire (.016 inch dia.) was used in making the thermal Ag/AgCl half-cells. Glass capillary tubing, .080" O.D. x .065" I.D. (in the form of calibrated 200 pipettes) was obtained from Coulter Diagnostics, Inc. NAFION is a copolymer of tetrafluoroethylene and monomers such as perfluoro-3,6-dioxo-4-methyl-7-octenesulfamic acid, yielding a structure such as the following:



where

$m=5$ to 13.5

$n=\text{Ca } 1,000$

$z=1, 2, 3 \text{ ---}$

95 Fabrication Procedure

1. Form a porous thermal Ag/AgCl contact on the end of a length of silver wire. This can be done by a dip-and-fire process using a 70/30 mixture of $\text{Ag}_2\text{O}/\text{AgClO}_2$. See Rule, C.K. et al., "Thermal Type Silver-Silver Chloride Electrodes" J. Amer. Chem. Soc. 58, 2339 (1936). The contact should be at least one inch long and large enough in diameter (around .9 mm) to fit snugly within the NAFION tube. NOTE: Porosity of the half-cell contact is desired for good performance and for vacuum filling of the contact as described below.

2. Cut about a 3/4 inch length of NAFION tubing. Surround the tubing with a small amount of 734 RTV silastic about one quarter of the way from an end. Push this end into the capillary tubing (using whatever tubing length is required to make the desired electrode). Slide the NAFION half-way into the capillary so that a good

concentric seal of silastic is formed between the interior surface of the capillary and the exterior surface of the NAFION. The boundary between the exterior NAFION and silastic should be even and just outside the end of the capillary. Allow the silastic to cure.

3. Insert the thermal contact so that the porous part protrudes slightly from the NAFION tube. The silver wire should protrude from the other end of the capillary. Clip the thermal contact even with the NAFION, and dip this end into the wet-patching epoxy so that all of the NAFION is covered except for a small ring (about 1 mm) between the epoxy and the silastic. This forms the annular window of NAFION which will connect the inner and outer solutions. Seal the other end of the tube (from which the silver wire protrudes) with epoxy or silastic. Allow to cure.

4. The half-cells are filled by a "vacuum technique". Clip off the very tip of the epoxy-covered NAFION, exposing the porous silver. Immerse the clipped end in AgCl-saturated 4M KCl, draw a full vacuum, then slowly release. The tube will fill through the porous silver. The glass tube should be completely full except for a small bubble at the top end. Allow the half-cells to sit in the solution for a while (e.g. 30 minutes) to ensure hydration. Then rinse the tip briefly in distilled water to remove salt, blot dry, and seal by redipping the tip in wet-patching epoxy. Allow to cure and store in a moist environment to prevent drying of the half-cells.

5. To activate the NAFION internals prior to utilization in electrodes, immerse the half-cells into pure 4M KCl at about 90° for about 10 minutes. The 4M KCl should be kept covered to prevent evaporation, as activation in a more concentrated electrolyte could change the internal KCl concentration slightly and cause temporary drift. This step could be eliminated, but it rapidly hydrates the membrane, bringing down the resistance of the internals to the low level desired, ensures a uniform result when electrode resistances are measured later during quality control, and ensures that leaks will not occur with later thermal cycling.

6. Integrity of the half-cells can be tested by applying a vacuum. They should not leak electrolyte. Half-cell resistances measured at room temperature should be a few hundred ohms.

7. The internals are now ready for use in fabricating electrodes. To prevent evaporation from the half-cell, finished electrodes should either be stored in a moist environment or be promptly filled with pure 4M KCl electrolyte. However, this is not too critical; the electrodes can certainly be kept dry for enough time (e.g. a few days) to allow routine fabrication, epoxy potting, etc.

From a theoretical standpoint, it is only necessary to select a suitable ion-selective barrier and position it between the electrochemical half-cell and the junction electrolyte for employment in the present invention. The invention has been illustrated with respect to preferred embodiments

thereof using a cationic exchange membrane with Ag/AgCl electrochemical half-cell and KCl junction electrolyte because in such a system, the silver ion will be complexed with chloride ion in the form of negatively-charged $\text{Ag}_n\text{Cl}_{n+1}^-$ complex or the like, which will be blocked by the cationic exchange membrane while potassium ion will be transported therethrough from the silver chloride-saturated potassium chloride half-cell electrolyte to the 4 Molar KCl junction electrolyte to provide electrical conduction.

Where it is desired to block a cation, such as mercury ion or thallium ion, an anionic exchange membrane would be employed to block passage of the cations while allowing anions, such as chloride, to pass through.

Ion-specific exchange membranes are known, such as Valinomycin for potassium ion, which would be operable in the present invention, such as where the specific exchange ion is found in both the half-cell electrolyte and the junction electrolyte, and ions other than the specific exchange ion are to be blocked. For example, Valinomycin would allow ionic conduction via K^+ , while blocking H^+ , Ti^+ , $\text{Ag}_n\text{Cl}_{n+1}^-$, and the like.

The ion-specific barrier must be inert to the environment of the reference electrode. Otherwise, many different types of anionic or cationic exchange and specific ion-exchange barriers could be employed. For example, barriers to block transport of anionic species could be fabricated from cation-exchange resins having carboxylic, phosphoric, sulfonic or similar acidic groups. Barriers to block transport of cationic species could be fabricated from anion exchange resins having amino, quaternary amine, or similar basic groups. Cast polyvinylchloride barriers containing potassium tetraphenylborate are K^+ specific, and could serve in place of Valinomycin membranes. Similar membranes containing organic exchanger for Cl^- would allow conductivity via Cl^- , while blocking other ions.

In preferred embodiments of the present invention, the ion-selective barrier material is characterized by a high permselectivity ratio between desired and undesired ionic species, because high selectivity reduces the electrical resistance required of the barrier to achieve the desired degree of blocking of undesired ions.

In preferred embodiments of the present invention, the ion-selective barrier is characterized by a low rate of water vapour transpiration, because water vapour transpiration tends, particularly at high temperatures, to dehydrate the half-cell electrolyte, changing ionic concentrations with a consequent drift in electrode potential.

In preferred embodiments of the present invention, the ion-selective barrier is also characterized by a low permeability to aqueous flow under pressure, because such flow tends to cause loss of half-cell electrolyte and contamination of the junction electrolyte as a consequence of fluctuations in ambient pressure and temperature.

Several attributes of NAFION perfluorosulfonic acid membrane make it a very preferred barrier material for use in Ag/AgCl reference electrodes. NAFION is extremely stable physically,

- 5 chemically, and thermally in the environment of the reference electrode. Also, NAFION exhibits a very high selectivity for K^+ over $Ag_nCl_{n+1}^-$ in concentrated KCl, which our experiments suggest is partially because the pores of NAFION are small enough to discriminate against the rather large $Ag_nCl_{n+1}^-$ complex on the basis of size as well as charge. NAFION is also quite impermeable to both aqueous flow and transpiration. Thus, the preferred embodiment of the present invention using NAFION membrane exhibited low resistance, very effective blocking of silver ion transport, and exceptionally stable potentials at elevated temperatures.

- Due to the charge selective nature of the barriers of the present invention, an electric potential develops across the barrier in response to a difference in concentrations of the transported ion(s) on the two sides of the barrier. Thus, in preferred embodiments of the present invention, essentially the same concentrations of transported ions are present on either side of the barrier, since this minimizes the barrier potential and reduces the tendency of the electrode potential to drift. However, in principle the concentrations of transported ions could be different on the two sides of the barrier. Realistically, however, the shifts and drifts in potential which would occur upon the use of significantly dissimilar electrolytes on the two sides the barrier would decrease the utility of the preferred embodiments of the present invention in achieving the same objective as conventional double junction electrodes; namely, electrical stability with a variety of junction electrolytes. Thus, while similar in configuration to prior art double junction electrodes, the electrodes of the present invention are not primarily intended or particularly suitable as replacements for conventional or prior art double junction electrodes.

- In actual practice, using a NAFION ion-selective barrier, with AgCl-saturated 4M KCl half-cell electrolyte and pure 4M KCl junction electrolyte, the Figure 2 embodiment exhibited some instability and small abrupt shifts in potential when physically disturbed during prolonged periods of heating at 90°C. This instability is caused partly by direct exposure of the membrane to the junction electrolyte, which becomes inhomogeneous after long heating, so that physical disturbance of the electrode caused abrupt changes in electrolyte concentration at the exposed membrane surface, resulting in abrupt shifts in potential across the NAFION membrane. To a lesser extent the same problem existed with the Figure 3 embodiment. The Figure 4 embodiment was very stable because the layers of filter paper 60 and cotton plug 52 served to isolate the ion-selective membrane 44 from abrupt changes in electrolyte concentration. The

Figure 5 embodiment was also found to be very stable in potential, possibly because the annular window and other details of the configuration allow a more uniform and stable contact to both electrolytes than afforded by a planar membrane configuration. Both the Figure 4 and Figure 5 embodiments drifted less than approximately one millivolt over seven days at 90°C.

- Variations of the present invention will be apparent to the skilled artisan. In particular, considerable variation is allowed in the nature of the ion-selective barrier which provides an ionic electrical pathway between the half-cell and junction electrolytes.

- While in present electrode terminology there is a clear distinction in meaning between "porous materials" as typically employed for reference electrode junctions and "ion-selective materials" are typically employed as ion-sensor membranes and the like, such materials in theory merely represent extremes in a continuum of possible properties. For example, porous junctions can be provided with varying degrees of ion specificity by the attachment of fixed ionic groups to the pore walls, whereas ion-selective barriers also can be porous on ionic or higher levels, e.g. as in cation-conductive membranes and beds of ion-exchange resin particles. The essential distinction between the porous junctions of the prior double junction art and the ion-selective barriers of the present invention, however, is the following: in the former, the pores have relatively little influence on the ions in solution, so that the ratios of the diffusional permeability of various ions through the junction are essentially the same as in the free solution, whereas in the latter the pores exert a significant differential effect on ionic mobility, so that the diffusional permeability ratios through the barrier are significantly altered from their values in free solution. Thus, a two-fold change in the ionic permeability ratio can be exploited to yield a two-fold reduction in barrier resistance, a significant advantage.

- For the purpose of describing the present invention, then, the term "ion-selective material" refers to any material which, when in contact with the electrolytes employed, imparts a diffusional permeability ratio for at least one pair of significant ions present in one or both electrolytes which varies by more than a factor of about two from the diffusional permeability ratio of the same ions in free solution. By "significant ions" is meant those ions which are related to electrode function, e.g. ions providing electrical conduction, causing junction clogging, contaminating the external sample, and the like. On the other hand, the term "porous material" as used herein refers to any material which does not alter the ionic permeability ratios as described above, regardless of the physical pore dimensions.

- The diffusional permeabilities of materials to various ions are easily determined by well-known dialysis techniques. As an example, I have determined the $Ag_nCl_{n+1}^-:K^+$ permeability ratio of a NAFION membrane in 4M KCl to be at least

100-fold lower than that observed through grossly porous junctions which are equivalent to columns of free solutions. The $\text{Cl}^-:\text{K}^+$ permeability ratio also was significantly decreased, as expected. Thus, to achieve a given degree of $\text{Ag}_n\text{Cl}_{n+1}^-$ blocking, the resistance required of a NAFION barrier is at least 50-fold lower than that required of a nonspecific porous barrier which does not alter the relative diffusion rates of the various ions.

Claims

1. A reference electrode having a double junction configuration and comprising: a first housing containing an electrochemical half-cell being electrically connectable to an external measuring means and consisting essentially of a half-cell electrode and a half-cell electrolyte, a second housing containing a junction electrolyte, an ion selective barrier which allows desired ion migration to maintain an ionic electrical pathway between said half-cell electrolyte and said junction electrolyte and which substantially prevents undesired ion migration, thereby substantially preventing contamination of said junction electrolyte with undesired ions, and a reference junction allowing ionic conduction between said junction electrolyte and an external sample to be measured.

2. A reference electrode as claimed in claim 1 wherein the ion-selective barrier is a cationic exchange membrane, whereby cations are exchanged by the membrane to provide ionic conduction between the electrochemical half-cell and the junction electrolyte while anions are substantially prevented from migrating from the half-cell electrolyte to the junction electrolyte.

3. A reference electrode as claimed in claim 1

wherein the ion-selective barrier is an anionic exchange membrane, whereby anions are exchanged by the membrane to provide ionic conduction between the electrochemical half-cell and the junction electrolyte while cations are substantially prevented from migrating from the half-cell electrolyte to the junction electrolyte.

4. A reference electrode as claimed in claim 1, wherein the ion-selected barrier is an ion-specific exchange membrane, whereby said specific ion is exchanged from the electrochemical half-cell to the junction electrolyte to provide ionic conduction between the electrochemical half-cell and the junction electrolyte while other ions are prevented from migrating from the electrochemical half-cell to the junction electrolyte.

5. A reference electrode as claimed in claim 2, wherein the electrochemical half-cell is a Ag/AgCl half-cell, the half-cell electrolyte is AgCl -saturated KCl and the junction electrolyte is KCl .

6. A reference electrode as claimed in claim 3 wherein the electrochemical half-cell is a calomel half-cell or a thallium based half-cell.

7. A reference electrode as claimed in any one of claims 1, 2, 3, 4, 5, or 6 wherein the ion-selective barrier is of a pore size sufficient to reduce physical migration of undesired ion(s) from the half-cell electrolyte to the junction electrolyte.

8. A reference electrode as claimed in any one of claims 1, 2, 3, 4, 5 or 6 in a combination electrode configuration.

9. A reference electrode as claimed in claim 7 in a combination electrode configuration.

10. A reference electrode substantially as described with reference to the accompanying drawings.